



**STATUTORY DECLARATION**

I, Hyun Soon KIM, a citizen of the Republic of Korea and a staff of Bae, Kim & Lee, do hereby declare that:

1) I am conversant with the English and Korean languages and am a competent translator thereof;

2) To the best of my knowledge and belief, the following is a true and correct translation of the Priority Document (No. KR Patent Application NO. 10-2003-22007) filed on April 8, 2003.

Signed this 14<sup>th</sup> day of April, 2005

*Hyun Soon Kim*

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Hyun Soon KIM

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[Attached Document] 1. Abstract and Specification (Drawings)\_1 copy

## [ABSTRACT]

### ABSTRACT OF THE DISCLOSURE

5 The present invention relates to a cleaning composition to remove  
a photoresist polymer after a dry etching or ashing process of a  
semiconductor manufacturing process. The cleaning composition  
comprises: (a) 5wt% to 15wt% of sulfuric acid, (b) 1wt% to 5wt% of  
hydrogen peroxide or 0.0001wt% to 0.05wt% of ozone, (c) 0.1wt% to  
10 5wt% of acetic acid, (d) 0.0001wt% to 0.5wt% of ammonium fluoride  
and (e) a remaining amount of water. During the dry etching and ashing  
process, photoresist reacts with etching and ashing gases, so that  
resist polymers generated on sidewalls and bottoms in a lower metal  
film or other films are easily removed by the cleaning composition.  
Specifically, the cleaning composition is useful to remove resist  
15 polymers on sidewalls and bottoms in lower metal films such as aluminum,  
aluminum alloy or tungsten, and also to minimize corrosion of the  
lower metal films in removal of photoresist polymers.

### REPRESENTATIVE FIGURE

20 Fig. 2

**[SPECIFICATION]**

**[TITLE OF THE INVENTION]**

MANUFACTURING METHOD OF SEMICONDUCTOR DEVICE

5

**[BRIEF DESCRIPTION OF THE DRAWINGS]**

10 <1> Fig. 1 is a SEM (Scanning Electron Microscope) photograph showing a photoresist pattern obtained by coating photoresist on a substrate comprising titanium nitride, aluminum and titanium sequentially and then treated with a dry etching process and an ashing process.

15 <2> Fig. 2 is a SEM photograph showing experimental results when photoresist polymers are removed at room temperature using a photoresist polymer remover composition of Example 1 according to an embodiment of the present invention.

<3> Fig. 3 is a SEM photograph showing experimental results when photoresist polymers are removed at room temperature using a photoresist polymer remover composition of Comparative Example 2.

20 <4> Fig. 4 is a SEM photograph showing experimental results of metal film corrosion at room temperature using the photoresist polymer remover composition of Example 1 according to an embodiment of the present invention.

25 <5> Fig. 5 is a SEM photograph showing experimental results of metal film corrosion at room temperature using a photoresist polymer remover composition of Comparative Example 1.

**[DETAILED DESCRIPTION OF THE INVENTION]**

**[OBJECTS OF THE INVENTION]**

**[FIELD OF THE INVENTION AND BACKGROUND ARTS]**

30 <6> The present invention generally relates to a photoresist polymer remover composition which effectively removes photoresist residuals generated from etching or ashing sub-processes in photoresist pattern forming processes during the manufacturing of semiconductor

devices such as high integrated circuit and ultrahigh integrated circuit.

<7> In a conventional semiconductor device manufacturing process, a photoresist pattern is formed on a conductive layer which has been formed on a semiconductor substrate. The conductive layer whose portion is not covered by the pattern is etched using the photoresist pattern as a mask to form a conductive layer pattern.

This lithography process is then repeated to form the conductive patterns. The photoresist pattern is used as the mask and it should be removed from the conductive layer with a photoresist remover in a strip process after the process for forming the conductive layer pattern is completed. However, it is difficult to remove photoresist material in the subsequent strip process since the etching process for forming a conductive layer pattern is performed with a dry etching process when making highly integrated devices and, as a result, the physical property of photoresist is deteriorated during the dry etching process.

<8> Dry etching processes have replaced wet etching processes which use liquid acid compositions. In dry etching, gas-solid phase reaction are generated between a plasma etching gas and a conductive layer. Since sharp patterns are obtained with dry etching processes and they are easy to control, dry etching processes are preferred to wet etching processes. However, during dry etching process, ions and radicals included in the plasma etching gas cause a complicated chemical reaction on the surface of a photoresist film which rapidly hardens the photoresist material. In addition, a "puffing" phenomenon occurs, thereby generating a residue of the photoresist material.

As a result, it is difficult to remove the photoresist material. Specifically, when the dry etching process is performed on metal conductive layers such as aluminum, aluminum alloy and titanium nitride, photoresist polymers on sidewalls of the metal conductive layer are chemically transformed and hardened. As a result, the resist polymers are not easily removed even by various removers in a strip process.

<9> The currently available remover compositions including organic amine compounds and various organic solvents that are also

used in the wet etching process. The available remover compositions typically include mono ethanolamine.

<10> However, in current semiconductor device manufacturing processes, the above remover does not fully remove the photoresist which is baked at high temperatures because various substrates such as silicon wafers are treated at a high temperature ranging from 110 to 140°C. The remover compositions containing water, hydroxyl amines or mixtures thereof have been developed for removing photoresist materials baked at high temperatures.

<11> Since the resist polymer is exposed to plasma gas in dry etching or ashing processes which are used for manufacturing ultra high integrated circuits, the remover compositions do not fully remove the resist polymers which is chemically transformed and hardened. As a result, development of photoresist removers to overcome the above-described problem is needed.

<12> A semiconductor substrate treated with the ashing process is conventionally heated at a high temperature of over 200°C. Here, residual solvent in the photoresist should be vaporized and exhausted.

However, a hardened layer which remains on the photoresist surface after the ashing process prevents exhaustion of the residual solvents.

As a result, the surface of the photoresist film can be broken or cracked by the residual solvent as internal pressure of the photoresist film increases during the ashing process, which is called a "puffing" phenomenon. Since the hardened layer shattered by the puffing phenomenon still remains on the photoresist material, it is difficult to remove the photoresist material with common removers. Such photoresist material is transformed into residues and particles, which may become pollutants and causes to lower yield rate in manufacture of ultra high integrated circuits. When the ashing process is performed before the strip process to remove the photoresist material, the transformation of the photoresist layer is deteriorated, which results in defects during the strip process.

<13> Of various ashing processes to effectively remove the above-described transformed and hardened photoresist material, the



two-step ashing process wherein the common ashing process is performed and then the second ashing process is re-performed is proposed (Fujimura, Japanese Spring Applied Physics Society Proceedings 1P-13, p. 574, 1989). However, since these processes are complicated and comprise large-scale equipment, their production yield is degraded.

<14> Only strip processes using compositions for removing photoresist polymers have been used. Of the compositions, recently proposed photoresist removers comprising hydroxyl amine, alkanol amine, corrosion inhibitor and water are extensively used because they are more effective to remove relatively transformed and hardened photoresist material. However, the above compositions do not fully remove photoresist polymers on metal lines or sidewalls of interlayer insulating films in production line of semiconductors such as DRAMs of 256M or more where new metal films are used for metal lines or new insulating materials used for interlayer insulating films. As a result, a photoresist remover to complement the above-described problem is also needed.

#### [TECHNICAL SUBJECT OF THE INVENTION]

<15> In order to solve the above-described problems, it is an object of the present invention to provide improved photoresist polymer remover compositions which effectively remove photoresist polymers formed on sidewalls and bottoms of lower films of the photoresist by dry etching or ashing processes in processes for forming metal lines, via hole patterns and other patterns. When the lower films are metal films, the disclosed photoresist polymer remover compositions minimize corrosion of the metal films.

#### [CONFIGURATION OF THE INVENTION]

<16> There is provided a photoresist polymer remover composition comprising (a) sulfuric acid, (b) hydrogen peroxide or ozone, (c) acetic acid, (d) ammonium fluoride and (e) water.

<17> Hereinafter, the present invention will be described in details

<18> The photoresist polymer remover composition comprises (a) 5wt% to 15wt% of sulfuric acid, (b) 1wt% to 5wt% of hydrogen peroxide or 0.0001wt% to 0.05wt% of ozone, (c) 0.1wt% to 5wt% of acetic acid, (d) 0.0001wt% to 0.5wt% of ammonium fluoride and (e) a remaining amount of water.

<19> The sulfuric acid is preferably present in an amount ranging from 5 to 15wt%, more preferably, from 7 to 10wt%. Photoresist polymer detergency may be degraded when the sulfuric acid is present in an amount of less than 5wt% while metal films may be corroded when the sulfuric acid is present in an amount of more than 15wt%.

<20> The hydrogen peroxide is preferably present in an amount ranging from 1 to 5wt%, more preferably, from 2 to 4wt%. Photoresist polymer detergency is degraded when the hydrogen peroxide is present in an amount of less than 1wt% while economic efficiency is degraded when the hydrogen peroxide present in an amount of more than 5wt%.

When ozone which is a strong oxidizer is used, photoresist residues may be effectively removed by the ozone of small concentration. The ozone is preferably present in an amount ranging from 0.0001 to 0.05wt%, more preferably, from 0.0002 to 0.001wt%. The photoresist polymer detergency of the disclosed solutions may be degraded when the ozone is present in an amount of less than 0.0001wt% while economic efficiency may be degraded when the ozone is present in an amount of more than 0.05wt%. The hydrogen peroxide and the ozone may be selectively used.

<21> The acetic acid is preferably present in an amount ranging from 0.1 to 5wt%, more preferably, from 0.5 to 2wt%. Photoresist polymer detergency may be degraded when the acetic acid is present in an amount of less than 0.1wt% while corrosion of metal films may be deepened when the acetic acid is present in an amount of more than 5wt%.

<22> The ammonium fluoride is preferably present in an amount ranging from 0.0001 to 0.5wt%, more preferably, from 0.01 to 0.05wt%. When the ammonium fluoride is present in an amount of less than 0.0001wt%, it is difficult to completely remove transformed photoresist polymers on sidewalls and bottoms of lower films by dry etching and

ashing processes in a pattern formation process. When the ammonium fluoride is present in an amount of more than 0.5wt%, HSQ (Hydrogen Silsesquioxane) films such as FOX (Flowable Oxide) films of stacked films in via hole patterns are corroded.

5 <23> The disclosed photoresist polymer remover composition also includes water, which is preferably pure water filtered through ion exchange resin, and more preferably ultra pure water having resistivity of 18 MΩ.

10 <24> There is also provided a method of manufacturing a semiconductor device where photoresist polymer residuals are removed using the disclosed remover composition.

<25> The above method comprises the steps of:

<26> (a) forming a photoresist pattern on an underlying layer which is formed on a semiconductor substrate;

15 <27> (b) etching the underlying layer using the photoresist pattern as an etching mask; and

<28> (c) cleaning the resulting structure with the disclosed remover composition to remove residual photoresist polymers.

20 <29> In the above process, the underlying layer is a metal film or an insulating film. Here, the metal film is preferably selected from the group consisting of aluminum, aluminum alloy, titanium, titanium nitride, tungsten, and combinations thereof. In case of stacked films, a stacked film comprising titanium nitride/aluminum /titanium from the lower to the upper portion is preferable. When  
25 the underlying layer is an insulating film, the insulating film preferably is a HSQ film. In generally, a metal film is formed under the insulating film.

<30> Any conventional photoresist polymers may be used for polymers included in the above photoresist.

30 <31> The etching process in the step (b) is a dry etching process, and may further comprise an ashing process to first remove a photoresist pattern after the dry etching process and before the step (c).

<32> The photoresist pattern is formed by a photolithography process. Here, an exposure light source may be ArF (193nm), KrF (248nm), F<sub>2</sub> (157nm), EUV (13nm), E-beam, X-ray or ion-beam. After and before exposure, a bake process is performed.

5 <33> The photoresist pattern may be an insulating film hole pattern or a metal line/space pattern.

<34> Instead of the photoresist pattern formation process using a mask, a dry etching process such as an etch-back process or CMP (Chemical Mechanical Polishing) process is performed to clean the  
10 exposed photoresist film using the disclosed remover composition.

<35> The cleaning process of the step (c) may be performed using single-type or batch-type equipment. Although the cleaning condition may be differentiated by states of the resist material to be removed, the resist material is soaked using chemicals at room temperature  
15 or below 60°C for about 10 to 60 seconds to completely remove photoresist polymers.

<36> The disclosed photoresist polymer remover composition may easily remove resist polymers formed on sidewalls and bottoms of the lower films of photoresist by dry etching or ashing processes  
20 in recent high-integrated circuit semiconductor device manufacturing process for manufacturing semiconductor device within a short time. When the lower film is an aluminium, aluminum alloy or tungsten, the photoresist polymer remover composition may effectively remove resist polymers formed on sidewalls of the photoresist pattern.

25 <37> The disclosed remover composition effectively removes photoresist polymers and minimizes corrosion of new lower metal films applied to yield line of ultra high integrated circuits such as DRAMs of over 256M. Also, the disclosed remover composition prevents an attack phenomenon on HSQ films such as FOX films of stacked films  
30 in the via hole pattern formation process.

<38> The disclosed photoresist polymer remover compositions will be described in more details by referring to examples below, which are not intended to be limiting.

<39>        Examples 1-5 and Comparative Examples 1-3 : Preparation of photoresist polymer remover composition

<40>        Each ingredient was mixed in ratios shown in the following table 1 to obtain photoresist polymer remover compositions of Examples 1-5 and Comparative Examples 1-3.

<41>        Table 1

<42>

|                        |   | Composition Ingredient (wt%) |                      |        |                       |                             |      |              |
|------------------------|---|------------------------------|----------------------|--------|-----------------------|-----------------------------|------|--------------|
|                        |   | (a)<br>Sulfuric<br>acid      | (b)                  |        | (c)<br>Acetic<br>acid | (d)<br>Ammonium<br>fluoride | HF   | (e)<br>Water |
|                        |   |                              | Hydrogen<br>peroxide | ozone  |                       |                             |      |              |
| Example                | 1 | 5                            | 5                    | -      | 2                     | 0.05                        | -    | Residue      |
|                        | 2 | 10                           | 3                    | -      | 2                     | 0.05                        | -    | Residue      |
|                        | 3 | 10                           | 5                    | -      | 0.5                   | 0.05                        | -    | Residue      |
|                        | 4 | 10                           | 5                    | -      | 2                     | 0.025                       | -    | Residue      |
|                        | 5 | 10                           | -                    | 0.0005 | 2                     | 0.05                        | -    | Residue      |
| Comparative<br>Example | 1 | 10                           | 5                    |        | 3                     | -                           | 0.05 | Residue      |
|                        | 2 | 10                           | 5                    |        | 3                     | -                           | -    | Residue      |
|                        | 3 | 10                           | 5                    |        | -                     | 0.05                        | -    | Residue      |

<43>        Performance evaluation on the remover compositions of the Examples and Comparative Examples was performed by the following methods of Experimental Examples.

<44>        Experimental Example 1. Removal of polymer

<45>        (1) Preparation of Test sample A

<46>        On an 8-inch silicon wafer where a titanium nitride film, an aluminum film and a titanium film were sequentially deposited from the lower to the upper portion at 100Å, 8000Å and 400Å, respectively, a conventional positive-type resist composition sold under the designation "DPR-i1000" by Dongjin Semichem Co. Ltd. was spin-coated to obtain a resist film of 1.01μm. Thereafter, the resist film was pre-baked on a hot plate at 110°C for 90 seconds. A mask having a

predetermined pattern was located on the resist film, and irradiated with ultraviolet rays. Then, the exposed resist film was developed at 21°C for 60 seconds by TMAH developing solution of 2.38wt% to form a photoresist pattern. A test sample where the photoresist pattern was formed was hard-baked at 120°C for 100 seconds on the hot plate.

The titanium nitride film, the aluminum film and the titanium film were etched using the photoresist pattern as a mask and  $\text{Cl}_2/\text{BCl}_3$  mixed gas as etching gas in dry etching equipment (Applied Multireal Co., Model : DPS+) for EPD (End Point Detection) +45 seconds. Then, the ashing process was performed to remove most of the photoresist material using  $\text{O}_2$  plasma, thereby obtaining Test sample A. Fig. 1 shows the cross-section of the Test sample A. Photoresist polymers still exist on sidewalls of the Test sample A.

#### <47> (2) Removal of resist polymer

<48> The Test sample A was soaked in each resist polymer remover composition of Examples 1-5 and Comparative Examples 1-3 at room temperature. The Test sample was washed with ultra pure water, and dehydrated with nitrogen gas. Then, whether resist polymer residuals were attached on sidewalls of the pattern and on the surface of the line pattern was examined by the Scanning Electron Microscope (SEM, Hitachi Co. Ltd., Model: S-5000) in order to evaluate resist polymer removal performance. The experimental results were shown in the following table 2, and Figs. 2 and 3.

<49> Table 2

<50>

|                     |   | Soaking Time |         |         |
|---------------------|---|--------------|---------|---------|
|                     |   | 15 sec.      | 30 sec. | 60 sec. |
| Example             | 1 | O            | O       | O       |
|                     | 2 | O            | O       | O       |
|                     | 3 | O            | O       | O       |
|                     | 4 | O            | O       | O       |
|                     | 5 | O            | O       | O       |
| Comparative Example | 1 | O            | O       | O       |
|                     | 2 | X            | X       | X       |

|  |   |   |   |   |
|--|---|---|---|---|
|  | 3 | X | X | Δ |
| O : resist residuals were completely removed on sidewalls and the surface of the line pattern<br>Δ : more than 80% of resist residuals were removed on sidewalls and the surface of the line pattern<br>X : most of resist residuals were not removed on sidewalls and the surface of the line pattern |   |   |   |   |

<51> Referring to Table 2, the polymer removal performance of Examples 1-5 and Comparative Example 1 was far superior to that of Comparative Examples 2 and 3.

5 <52> Figs. 2 and 3 are SEM photographs showing experimental results when photoresist polymers are removed using the photoresist polymer remover compositions of Example 1 and Comparative Example 2, respectively. The photoresist polymers were completely removed using the remover composition of Example 1 (see Fig. 2) while the  
10 photoresist polymers were not completely removed using the remover composition of Comparative Example 2 (see Fig. 3).

<53> Experimental Example 2. Corrosion of metal film

<54> (1) Preparation of Test sample B

<55> The procedure of Example 1 was repeated to obtain Test  
15 sample B.

<56> (2) Experiment of metal film corrosion

<57> The Test sample B was soaked in each photoresist polymer remover composition of Examples 1-5 and Comparative Examples 1-3 at room temperature. The Test sample was washed with ultra pure water  
20 and dehydrated with nitrogen gas. Then, whether an undercut phenomenon occurred in the lower metal film was examined by SEM to show corrosion degree of the lower metal film. The corrosion degree was shown in the following table 3.

<58> Table 3

25 <59>

|   |   | Soaking Time |        |        |
|---|---|--------------|--------|--------|
|   |   | 1 min.       | 3 min. | 5 min. |
| Example   | 1 | O            | O      | O      |
|   | 2 | O            | O      | O      |
|   | 3 | O            | O      | O      |
|   | 4 | O            | O      | O      |
|   | 5 | O            | O      | O      |
| Comparative Example   | 1 | X            | X      | X      |
|   | 2 | O            | O      | O      |
|   | 3 | O            | O      | O      |
| O : when the undercut phenomenon did not occur in the lower metal film      |   |              |        |        |
| Δ : when the undercut phenomenon partially occurred in the lower metal film |   |              |        |        |
| X : when the undercut phenomenon severely occurred in the lower metal film  |   |              |        |        |

<60> As shown in Table 3, the undercut phenomenon did not occur in the lower metal film after 5 minutes of the soaking time in Examples 1-5. However, in Comparative Example 1, the undercut phenomenon severely occurred in the lower metal film even the Test sample B was soaked for 1 minute. Although the experimental results of metal film corrosion were positive in Comparative Examples 2 and 3, most resist polymer residuals were not removed on sidewalls and the surface of the line pattern as shown in Table 2. Accordingly, the remover composition of Comparative Examples 2 and 3 are not useful.

<61> Figs. 4 and 5 are SEM photographs showing experimental results of metal film corrosion at room temperature using a remover composition of Example 1 and Comparative Example 1, respectively.

The undercut phenomenon did not occur in the lower metal film when the remover composition of Example 1 was used (see Fig. 4). However, the undercut phenomenon severely occurred in the lower metal film when the remover composition of Comparative Example 1 was used (see Fig. 5).

<62> Experimental Example 3. Application to production line



<63> The evaluation results of a disclosed remover composition applied to semiconductor device production line are shown in the following tables 4 (hole pattern forming process) and 5 (line pattern forming process).

5 <64> Table 4

<65>

| Device/Process                           | Evaluation Item   | Evaluation Result  |
|--|---|--|
| 64MSD G<br>/Process1 Post-Cleaning       | Polymer removability  | Completely removed   |
|  | Sidewall film (HSQ) attack                                    | None   |
|  | Titanium nitride film attack                                  | None   |
|  | Foreign substance test on run<br>(KLA foreign substance test) | No specific foreign substance,<br>No plug missing              |
|  | PT1(Probe Test)/PCM(Process Control Monitoring Test)          | No significant difference compared to the conventional remover |
|  | WFBM(Wafer Fail Bit Map)<br>→ M2C related fail                | No related fail  |
|  | PKG Test  | No significant difference compared to the conventional remover |
|  |   |  |
| 256M DDR (BC)<br>/Process1 Post-cleaning | Polymer removability  | Completely removed   |
|  | Sidewall film (HSQ) attack                                    | None   |
|  | Titanium nitride film attack                                  | None   |
|  | Foreign substance test on run<br>(KLA foreign substance)      | No specific foreign substance                                  |
|  |   |  |

|  |  |  |
|--|--|--|
|  | PT1 (Probe Test) / PCM<br>(Process Control<br>Monitoring Test) | No significant<br>difference compared to<br>the conventional remover |
|--|--|--|

<66> The detailed process represented in Table 4 is as follows.

<67> (64MSD G/ Process 1 Post-cleaning)

<68> (1) A titanium film and a titanium nitride film were formed on a semiconductor substrate at 200Å and 800Å, respectively. (2) A tungsten (W) was formed on the resulting structure at 4000Å. (3) The tungsten was dry-etched by an etch-back process in dry-etching equipment using SF<sub>6</sub> gas. (4) A titanium film, an aluminum-copper film and a titanium nitride film were formed on the resulting structure at 100Å, 8000Å and 400Å, respectively. (4) A photoresist pattern was formed on the resulting structure. (5) The metal line was dry-etched using the photoresist pattern as a mask in dry-etching equipment using BCl<sub>3</sub>/Cl<sub>2</sub> gas, and consecutively the photoresist film was removed using O<sub>2</sub>/CF<sub>4</sub>/H<sub>2</sub>O gas. (6) The wafer was treated with the disclosed remover composition at 30°C for 30 seconds while the wafer was rotated with single type wet cleaning equipment at 400RPM (revolutions per minute). Then, the resulting wafer was washed with ultra pure water for 60 seconds, and dehydrated using a spin dry at 2900RPM for 30 seconds. The experimental results were shown in Table 4.

20 <69> (256M DDR(BC) / Process 1 Post-cleaning)

<70> (1) A titanium film and a titanium nitride film were formed on a semiconductor substrate at 200Å and 100Å, respectively. (2) A tungsten (W) was formed on the resulting structure at 4000Å. (3) A titanium film, an aluminum-copper film, a titanium film and a titanium nitride film were formed on the resulting structure at 100Å, 4000Å, 100Å and 750Å, respectively. (4) A photoresist pattern was formed on the resulting structure. (5) The metal line was dry-etched using the photoresist pattern as a mask in dry-etching equipment using BCl<sub>3</sub>/Cl<sub>2</sub> gas, and consecutively the photoresist film was removed using O<sub>2</sub>/CF<sub>4</sub>/H<sub>2</sub>O gas. (6) The wafer was treated with the disclosed remover composition at 30°C for 30 seconds while the wafer was rotated with

single type wet cleaning equipment at 400RPM. Then, the resulting wafer was washed with ultra pure water for 60 seconds, and dehydrated using a spin dry at 2900RPM for 30 seconds. The experimental results were shown in Table 4.

5 <71> Table 5

<72>

| Device/Process                             | Evaluation Item  | Evaluation Result  |
|--|--|--|
| 256M DDR(BC)<br>/Process2<br>Post-cleaning | Corrosion  | No corrosion   |
|  | Polymer removability                                       | Completely removed   |
|  | Sidewall film (metal such as Al) attack and undercut       | None   |
|  | Lower IMD (Inter Metal Dielectric) film attack             | None   |
| 128M DDR(BC)<br>/Process3<br>Post-cleaning | Corrosion  | No corrosion   |
|  | Polymer removability                                       | Completely removed   |
|  | Sidewall film (metal such as Al) attack and undercut       | None   |
|  | Lower IMD (Inter Metal Dielectric) film attack             | None   |
|  | Foreign substance test on run (KLA foreign substance test) | No specific foreign substance                                  |
|  | PT1 (Probe Test)/PCM (Process Control Monitoring Test)     | No significant difference compared to the conventional remover |

<73> The detailed process represented in Table 5 is as follows.

<74> (256M DDR(BC)/Process2 Post-cleaning)

10 <75> (1) A titanium film and a titanium nitride film were formed on a semiconductor substrate at 200Å and 800Å, respectively. (2) A tungsten (W) was formed on the resulting structure at 4000Å. (3) The tungsten was dry-etched by an etch-back process in dry-etching equipment using SF<sub>6</sub> gas. (4) A titanium film, an aluminum-copper

film and a titanium nitride film were formed on the resulting structure at 100Å, 8000Å and 400Å, respectively. (4) A photoresist pattern was formed on the resulting structure. (5) The metal line was dry-etched using the photoresist pattern as a mask in dry-etching equipment using  $\text{BCl}_3/\text{Cl}_2$  gas, and consecutively the photoresist film was removed using  $\text{O}_2/\text{CF}_4/\text{H}_2\text{O}$  gas. (6) The wafer was treated with the disclosed remover composition at 30°C for 30 seconds while the wafer was rotated with single type wet cleaning equipment at 400RPM. Then, the resulting wafer was washed with ultra pure water for 60 seconds, and dehydrated using a spin dry at 2900RPM for 30 seconds. The experimental results were shown in Table 5.

<76>        (128M DDR(BC)/Process3 Post-cleaning)

<77>        (1) A titanium film and a titanium nitride film were formed on a semiconductor substrate at 200Å and 100Å, respectively. (2) A tungsten (W) was formed on the resulting structure at 4000Å. (3) A titanium film, an aluminum-copper film, a titanium film and a titanium nitride film were formed on the resulting structure at 100Å, 4000Å, 100Å and 750Å, respectively. (4) A photoresist pattern was formed on the resulting structure. (6) The metal line was dry-etched using the photoresist pattern as a mask in dry-etching equipment using  $\text{BCl}_3/\text{Cl}_2$  gas, and consecutively the photoresist film was removed using  $\text{O}_2/\text{CF}_4/\text{H}_2\text{O}$  gas. (6) The wafer was treated with the disclosed remover composition at 30°C for 30 seconds while the wafer was rotated with single type wet cleaning equipment at 400RPM. Then, the resulting wafer was washed with ultra pure water for 60 seconds, and dehydrated using a spin dry at 2900RPM for 30 seconds. The experimental results were shown in Table 5.

<78>        Referring to Tables 4 and 5, when the disclosed remover composition is applied to the actual production line, photoresist polymers are shown to be completely removed using the disclosed remover composition. Additionally, the problems such as corrosion, sidewall attack and undercut which are caused the residual polymers after cleaning are not shown.

**[EFFECT OF THE INVENTION]**

<79> As discussed earlier, the disclosed photoresist polymer remover compositions may easily remove resist polymers formed on sidewalls and bottoms of the lower films of the photoresist by dry etching or ashing processes in processes for forming metal lines, via hole patterns and other patterns within a short time. When the lower films are metal films, the photoresist polymer remover compositions may minimize corrosion of the metal films.

[WHAT IS CLAIMED IS]

1. A method of manufacturing a semiconductor device comprising a process of forming a photoresist pattern using a photoresist polymer remover composition, said composition comprising: (i) 5wt% to 15wt% of sulfuric acid; (ii) 1wt% to 5wt% of hydrogen peroxide or 0.0001wt% to 0.05wt% of ozone; (iii) 0.1wt% to 5wt% of acetic acid; (iv) 0.0001wt% to 0.5wt% of ammonium fluoride; and (v) a remaining amount of water.

2. The method according to claim 1, said composition comprising: (i) 7wt% to 10wt% of sulfuric acid; (ii) 2wt% to 4wt% of hydrogen peroxide or 0.0002wt% to 0.001wt% of ozone; (iii) 0.5wt% to 2wt% of acetic acid; (iv) 0.01wt% to 0.05wt% of ammonium fluoride; and (v) a remaining amount of water.

3. The method according to claim 1, wherein the composition is further characterized as a dry etching cleaner.

4. The method according to claim 1, wherein the process of forming a photoresist pattern comprises the steps of:

(a) forming a photoresist pattern on an underlying layer which is formed on a semiconductor substrate;

(b) etching the underlying layer using the photoresist pattern as an etching mask; and

(c) cleaning the resulting structure using the photoresist polymer remover composition comprising (i) 5wt% to 15wt% of sulfuric acid; (ii) 1wt% to 5wt% of hydrogen peroxide or 0.0001wt% to 0.05wt% of ozone; (iii) 0.1wt% to 5wt% of acetic acid; (iv) 0.0001wt% to 0.5wt% of ammonium fluoride; and (v) a remaining amount of water to remove residual photoresist polymers.

5. The method according to claim 4, wherein the underlying layer is selected from the group consisting of aluminum, aluminum alloy, titanium, titanium nitride, tungsten, and combinations thereof.

5 6. The method according to claim 5, wherein the underlying layer is a stacked film where a titanium nitride film, an aluminum film and a titanium film are sequentially deposited.

10 7. The method according to claim 4, wherein the underlying layer is an insulating film, and a metal film is formed under the insulating film.

8. The method according to claim 7, wherein the underlying layer is a HSQ (Hydrogen Silsesquioxane).

15 9. The method according to claim 4, further comprising the step of removing the photoresist pattern by an ashing process after the etching process of the step (b) and before the cleaning process of the step (c).

20 10. The method according to claim 4, wherein the photoresist pattern is formed by a photolithography process using ArF (193nm), KrF (248nm), F<sub>2</sub> (157nm), EUV (13nm), E-beam, X-ray or ion-beam as an exposure light source.

25 11. The method according to claim 4, wherein said underlying layer pattern is an insulating film hole pattern or metal line/space pattern.

12. The method according to claim 4, wherein the photoresist pattern is formed by an etch-back process or CMP (Chemical Mechanical Polishing) process.

5 13. The method according to claim 4, wherein the cleaning process of the step (c) is performed using single-type or batch type equipment.

14. A semiconductor device manufactured by the method of claim  
4.